## Morphology Control of thin Copolymer Films by Nano-Particles

Lenin Singh Shagolsem

### Objectives:

The mixing of polymers and nanoparticles is opening pathways for the engineering of fexible composites that exhibit advantageous electrical, optical, and mechanical properties. For example, mixtures of biblockcopolymers and nano-particles produce highly ordered and complex composite structures which can serve as a next generation catalysts, selective membranes and photonic band gap materials. This is due to the block-copolymers' ability to self-organize into various morphologies and the fillers' ability to modify/improve the polymer properties thus producing polymer material with desired chemical/physical properties. In this project composite materials made of diblock-copolymers and nano-particles will be investigated using Molecular Dynamics simulations and theoretical approaches. In particular, we will focus on the morphology control of block-copolymer thin-films by adding selective and non-selective nano-particles. Using meanfield approaches, uptake of nano-particles in the copolymer matrix and the wetting/dewetting behavior of the copolymer film in the presence of nano-particles will be investigated. We will also consider magnetic nano-particles which have the potential to control and improve the block-copolymer morphologies in external magnetic field. Further, the effect of shear on the morphology of copolymer nano-composites will be considered.

### Outline of the work plan:

In the proposed PhD studies, considering a thin-film geometry, we will investigate the phase and order behavior of diblock-copolymer and nanoparticle mixtures both in equilibrium and non-equilibrium conditions. We will employ both the Molecular Dynamics (MD) simulation and analytical calculation (mean field approaches) to understand the behavior of copolymer/nanoparticle mixtures. For the simulations we will use a MD simulation package LAMMPS [1], and it is already applied succesfully in the studies of polymer brushes [2] and crystallization process in polymers [3] to mention a few. Moreover, the mixing of non-selective nano-particles and diblock-copolymers in a confined geometry has been studied using this method [4].

We will simulate selective nano-particles which prefers one of the copolymer phase in a confined geometry and study various morphologies of the nano-composite. The uptake of nanoparticles leads to a shift in the phase diagram and can cause morphological changes such as transition from cylinder-forming to lamellar-forming

nano-structures. Beside morphological transitions, in a confined geometry orientation of copolymer phases can be driven by the nano-particle uptake. Apart from this, using a simplified mean-field approache, we will address the issue of lamellar commensurability; also, by considering a preferential interaction between the substrate/vacuum and one of the copolymer phase we will study the wetting/dewetting transition of the polymer film. On the other hand, in non-equilibrium situation, we will simulate the influence of external shear deformation on the morphology of copolymer/nano-particle mixed system.

We will further consider ferro-magnetic nano-particles in an external magnetic field. Here, the nano-particles tend to form regular arrangements e.g., a string of nano-particles formed due to the dipole-dipole interaction, in the copolymer matrix. We can use such properties of the magnetic nano-particles to reorient the copolymer morphologies.

[1] Large-scale Atomic/Molecular Massively Parallel Simulator (http://lammps.sandia.gov)
[2] H. Merlitz, G.L. He, C.-X- Wu, and J.-U. Sommer, Phys. Rev. Lett., 102(11), 115702 (2009).
[3] C.-F. Luo and J.-U. Sommer, Phys. Rev. Lett., 102, 147801(2009); Macromolecules, 44, 1523(2011).
[4] Lenin S. Shagolsem and Jens-Uwe Sommer, Macromol. Theory and Simulations, 20, 329-339 (2011).